

STABILITY AND COMPATIBILITY TESTING USING A MICROCALORIMETRIC METHOD

C.J. ELMQVIST, P.E. LAGERKVIST and L.G. SVENSSON

AB Bofors, Department KPK, Box 500, S-691 80 Bofors, Sweden

ABSTRACT

A microcalorimetric method is used for compatibility and stability studies. The high sensitivity of the instrument permits measurements at 60°C or even lower, i.e. under more realistic conditions than offered by conventional techniques like DTA and vacuum stability tests. The instrument consists of four independent calorimeters with a short thermal relaxation time, high sensitivity and excellent baseline stability. The calorimeters are placed in a common, precisely thermostated water bath.

In compatibility studies, heat flow curves are recorded for the pure components and a mixture of these. A theoretical curve is constructed, which simulates a non-interacting system. The difference between the theoretical and the experimental curve for the mixture reflects the degree of interaction between the materials. A number of compatibility problems are discussed, including interactions in mixtures of TNT with amine/amide type polymers, polycarbonate - double base propellant interactions under various conditions and the influence of an anaerobic sealant on a high explosive and a propellant. Some results from stability measurements on an igniting compound are also presented.

INTRODUCTION

Many products - among them ordnance products - consist of numerous parts manufactured from a wide variety of materials, e.g. explosives, plastics and metals. These materials must not affect each other, as changed material properties may cause problems regarding safety or function of the product. If materials are acceptable in this respect, they are referred to as compatible in the product under consideration.

Interactions - chemical or physical - between materials are representing a wide range of reaction types and rates. An extreme case of incompatibility is found between TNT and a strong base, e.g. an amine. This interaction is obvious enough to be established even without the use of measuring techniques. The other extreme case is the 'long-term' incompatibility, characterized by a very slow reaction which has negligible influence on the properties of the compounds over a short

period of time, but which causes serious changes in material characteristics during several years of storage. Compatibility problems are not seldom the limiting factor for the shelf life of a product.

Several methods suitable for compatibility studies are known, e.g. DTA (ref. 1), vacuum stability test (refs. 2,3) and similar techniques (ref. 4), calorimetric methods (refs. 5-7) and accelerated storage followed by function testing or chemical analysis (ref. 3). No single method can however cope with all compatibility problems.

Microcalorimetry is a powerful new technique for stability and compatibility studies. Due to its high sensitivity, measurements could be carried out at much lower temperatures (60°C or less) than with conventional methods. This reduces extrapolation errors when the results are transferred to normal temperature conditions. Furthermore, the sensitivity makes it possible to detect very slow reactions in incompatible systems and in the decomposition of propellants and explosives. If no activity is detected in a sample, it is considered as stable. There is of course a theoretical chance for the occurrence of simultaneous reactions with perfectly balancing enthalpies, but this case is very improbable and may be neglected. In this paper we present microcalorimetric results for combinations of high explosives or propellants with a number of different polymers. A stability study of a pyrotechnic composition is also included.

EXPERIMENTAL

The microcalorimeter

The microcalorimeter used in this work is a prototype of a commercially available instrument, originally designed for biological measurements. It is developed and built at the Thermochemistry Laboratory, Chemical Center, University of Lund, Sweden. It consists of 4 independent calorimeters of twin type, placed in a common, precisely thermostated water bath, electronic equipment for signal amplification, calibration and temperature control and a pump plus heat exchanger for the water bath. The calorimeters are of the thermopile heat conduction type. Some data for the instrument are summarized in Table 1. A detailed description of the calorimeter is given elsewhere (ref. 8). A mini-computer is connected to the instrument to facilitate data collection, evaluation, plotting of results and direct readout of heat flow. The complete calorimeter system is shown in Figure 1.

Sample preparation

A survey of the materials used in this work is shown in Table 2. All materials were used without further purification. Before preparation of the microcalorimeter samples, the high explosives A1 and A3 were finely ground in a wooden grinding mortar. The propellant A5 and the polymers B1, B2, B4-B6 and B8 were ground in a Retsch type ZM1 high speed centrifugal mill. The remaining materials were used as received.

TABLE 1

Selected technical data for the microcalorimeter

<u>Water bath</u>	
Thermostat stability (at 37°C)	$\pm 1 \cdot 10^{-4} \text{°C}$ (24 h period)
Temperature range	45 - 95°C (20 - 80°C) ^a
<u>Calorimeter unit (for insertion vessels)</u>	
Baseline stability (at 37°C)	0.1 μW (12 h period)
Linearity (4 - 14000 μW)	Within 0.2%
Sample vessels ^b	Steel ampoule, volume 5 ml Glass vial, volume 3 ml
Thermal equilibration time ^c	45 min

^aFigures in paranthesis refer to the commercial version.

^bA perfusion - titration vessel is also available.

^cFrom 25°C (ambient) to 37°C (calorimeter temperature), steel ampoule with 5 ml water, no dynamic correction of the signal.

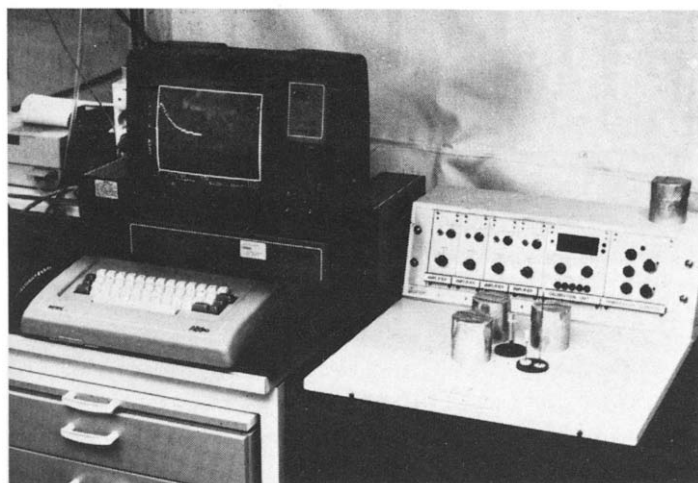


Fig. 1. The microcalorimeter with computer for data collection, evaluation, plotting and direct readout of heat flow (plotter is not shown here). A sample has just been removed from one of the calorimeters. The recovery curve of the empty calorimeter is shown on the screen.

TABLE 2

List of materials participating in this study

Nr	Sample	Manufacturer	Remarks
A1	TNT	Bofors	Technical grade
A2	RDX	Bofors	Recrystallized
A3	Composition B	Bofors	60±2% RDX, 40±2% TNT, technical grade
A4	Propellant I	Bofors	Double base
A5	Propellant II	-	Double base, pre-aged 250 days at +60°C
A6	Igniting composition	Bofors	KClO ₄ , B, Ba(NO ₃) ₂ , chlorinated rubber
B1	Nylon 6.6	Montedison	Polyamide 6.6
B2	Trogamid T	Dynamit Nobel	Aromatic polyamide (amorphous)
B3	Kevlar 49	DuPont	Aramide fiber (yarn)
B4	Araldite F/ Versamide 125	Ciba-Geigy/ Sclerling	DGEBA epoxy resin/ polyaminoamide
B5	Foss Than 750/956	Sadofoss	Polyol/MDI urethane adhesive
B6	Kapton	DuPont	Polyimide film
B7	Loctite 290	Loctite Ireland Ltd	Anaerobic acrylate adhesive/ sealant
B8	Makrolon	Bayer	Bisphenol A Polycarbonate

In all experiments we used 3 ml glass vials as sample vessels. The amount of sample was varied between 0.3 and 1.5 grams, depending on the densities of the materials. All samples were conditioned in a desiccator with controlled relative humidity (49%) at room temperature for 2 days. The vials were then sealed with a circular glass disc glued directly on the opening, using a UV-curing adhesive (Loctite 358). This sealing technique yields a very tight vessel with a minimum of polymeric sealant present.

In all experiments 1.5 grams of sea sand, purified by acid and calcined, was used as inert reference substance for the twin calorimeter.

Calorimeter measurements

The calorimetric data are presented as heat flow or integrated heat flow (energy) curves versus time, normalized to unit sample weight. Heat flow data are plotted for the pure components as well as for the mixture. A theoretical linear combination curve of the two pure compounds is constructed. This represents the ideal case of non-interacting components. The difference between the constructed and experimental curves reflects the degree of interaction in the system. All measurements were made at 70.0°C.

RESULTS AND DISCUSSION

In view of the previously mentioned reactivity of TNT with amines, incompatibility is expected when this explosive is exposed to polymers with similar functional

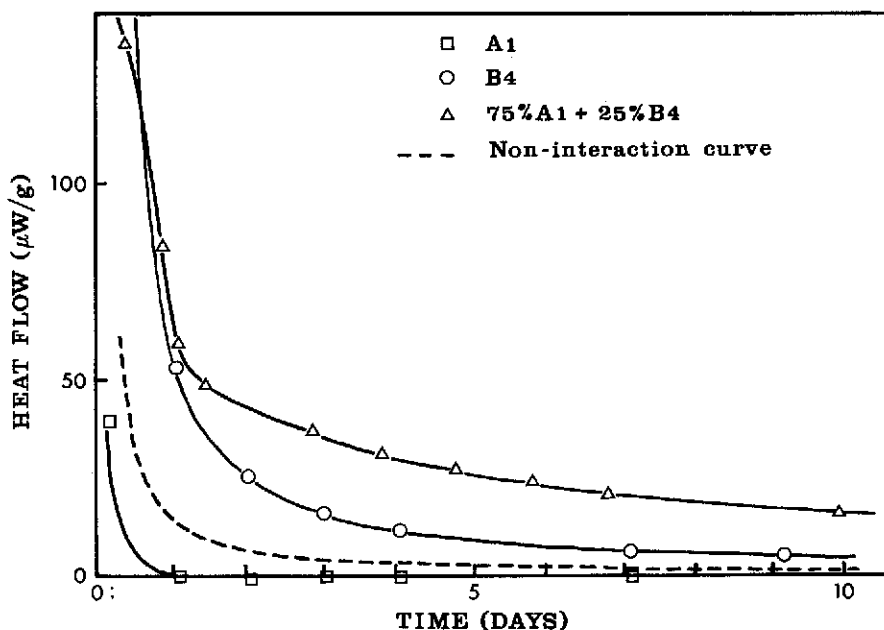


Fig. 2. Heat flow curves at 70°C for the TNT (A1)/epoxy (B4) system.

groups. In the first example we present microcalorimetric results for a number of such TNT/polymer systems. These include amine, amide, imide and urethane type polymers (samples B1-B6). Heat flow curves are discussed in detail for one of these systems, TNT/epoxy (A1/B4), see Fig. 2. During the first day of measurement, the pure components as well as the mixture are strongly exothermal. Such effects are frequently encountered in microcalorimetry, and are not specific for this system. Relaxation and equilibration processes initiated at the elevated temperature (70°C) contribute to these effects. As there are complications with the interpretation of these parts of the curves, they will not be considered in subsequent discussions.

The TNT curve decreases rapidly to zero heat flow, verifying the excellent stability of this compound. The epoxy curve decreases also, but is still exothermal after 10 days. The principal part of this exotherm originates from post-cure reactions. The dotted line is the theoretical non-interaction curve for a 75/25 wt% mixture of A1 and B4. A comparison with the corresponding experimental curve gives evidence of an interaction between the components. By computing the time integral of the difference between these two curves (starting at $t = 1$ day), we obtain a direct measure of the interaction energy. The result is shown in Fig. 3. The A1/B4 interaction amounts to 20 J/g after 9 days. If we assume, that the extrapolated energy at infinite time is at least 30 J/g , and that interactions between solid particles are

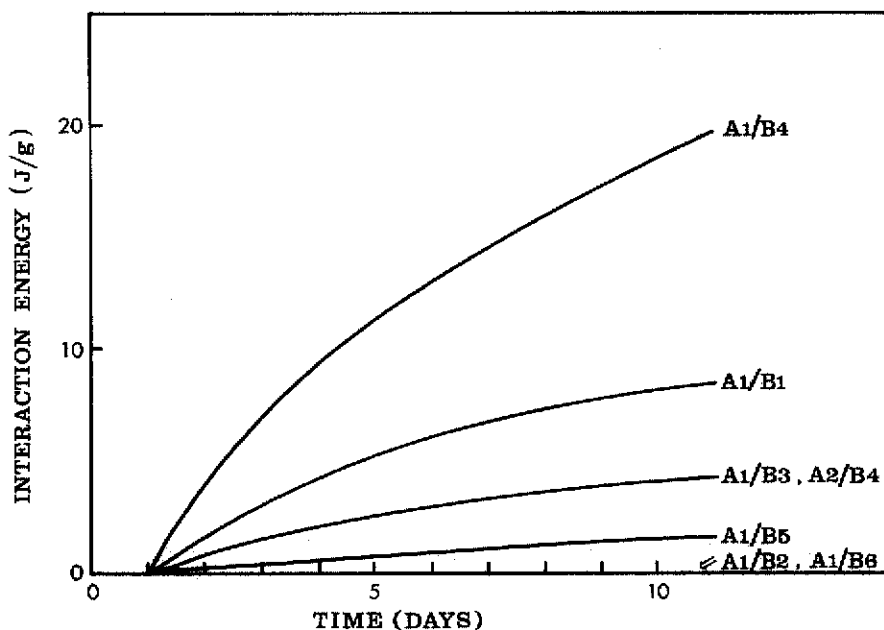


Fig. 3. Interaction energies at 70°C for the systems TNT (A1)/B1-B6 and RDX (A2)/B4.

limited to a surface region - say 20% of the particle volume - then the energy would roughly be 50 kJ/mole of TNT. Interactions of that magnitude are most likely to be of a chemical nature, and the system should be classified as incompatible.

Fig. 3 summarizes interaction energies for all TNT/polymer systems B1-B6. The largest energy is obtained for the B4 system. This polymer is the only one containing amino functional groups. Samples B1-B3 are pure amide type polymers. These exhibit varying degrees of interaction, all however of a lower magnitude than B4. This result is not surprising in view of the less nucleophilic nature of amides as compared to amines. The A1/B2 is very stable. This amide polymer contains bulky alkyl groups substituted on the polymer backbone to prevent crystallization of the material. The interaction with TNT is possibly sterically hindered by these groups. A moderate interaction is obtained with the B5 (urethane) material, while the B6 (imide) sample is not affected by TNT. The result for B6 is in accordance with the good chemical stability of the imide bond.

Fig. 3 also gives a comparison of the compatibility of the systems TNT/B4 and RDX/B4. RDX, representing a class of non-aromatic nitro compounds, appears to give the more stable system.

Experiences from material testing in our laboratory have shown that the mechanical properties of polycarbonate may be strongly affected by propellants. The chemical

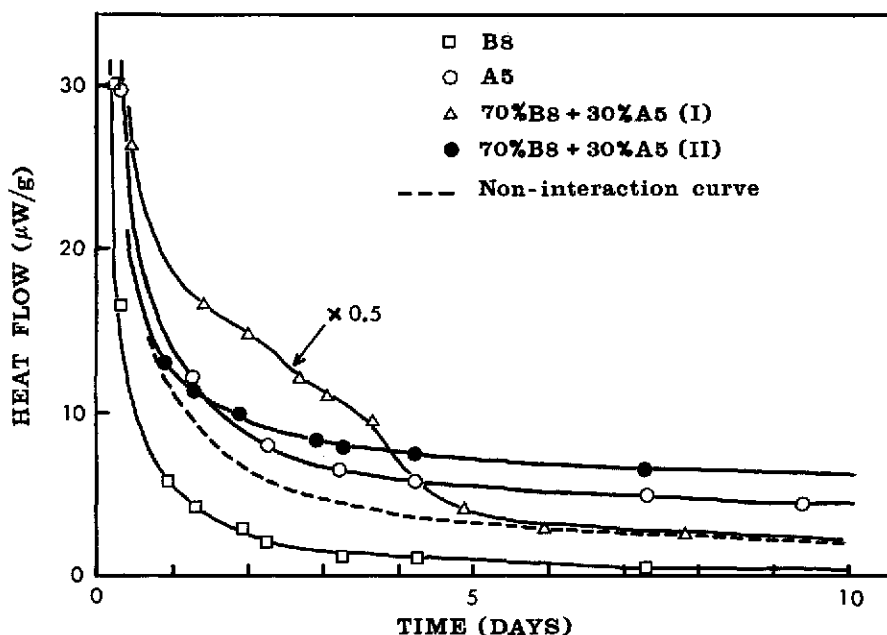


Fig. 4. Heat flow curves at 70°C for the system polycarbonate (B8)/double base propellant (A5). Note that curve I is reduced to half size.

activity leading to the polymer destruction has been studied with microcalorimetry. The result is displayed in Fig. 4 for the system A5/B8. The stability of the pure polymer is good, as shown by the small exotherm, curve B8. The propellant, curve A5, is slightly exothermal as expected, due to the spontaneous decomposition processes. Curve I illustrates the activity in a mixture containing 30 wt% of the propellant. A strong initial interaction is observed, which levels off rapidly. A considerable part of the reaction occurs obviously during the first week of exposure. Integration of the interaction between 1 and 10 days yields approximately 10 J/g of polymer, but the true energy is probably larger, with regard to the initial exotherm. If it is assumed that the interaction derives only from a chain scission reaction with an enthalpy approximated to 100 kJ/mole of monomer, then 10 J would correspond to degradation of 2.5% of the monomer-monomer bonds. That degree of degradation is most likely accompanied by altered mechanical properties. Curve II refers to a A5/B8 sample with the same composition ratio, but with the components separated by an inert fluorinated polymer. Also in this case we notice an interaction, however at a lower intensity. The result shows that the polymer destruction to a certain extent is caused by volatile compounds from the propellant, presumably various derivatives of the stabilizer.

The compatibility of the propellant A4 and the high explosive A3 with a standard

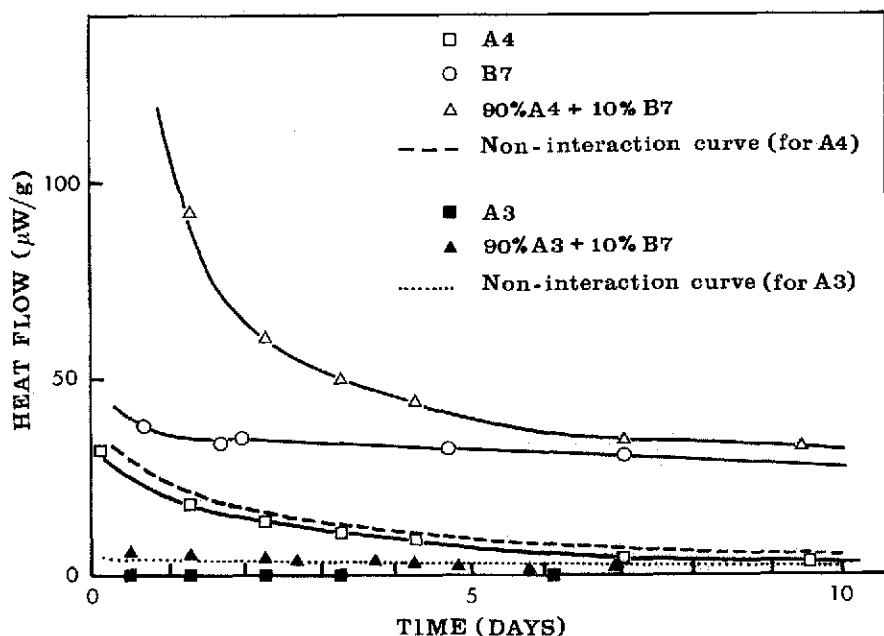


Fig. 5. Heat flow curves at 70°C for the systems B7 (anaerobic adhesive)/A3 (Comp. B) and B7/A4 (double base propellant).

anaerobic adhesive B7 has been investigated with microcalorimetry. Both systems are shown in Fig. 5. A marked difference in activity is observed between the A3/10 wt% B7 and A4/10 wt% B7 systems. The former exhibits good compatibility while the propellant exotherm increases considerably in the presence of adhesive. The interaction energy for A4/B7 integrated over 1 to 9 days is found to be 33 J/g sample. With that interaction magnitude, the system must be classified as incompatible. The chemical mechanisms behind the strong interaction are not known. However, the exothermal B7 curve shows that the pure adhesive undergoes a slow curing process, which produces traces of free radicals. These may possibly interfere with the radical reactions involved in the propellant decomposition.

We will finally show some results from a microcalorimetric study of the stability of an igniting composition A6, shown in Fig. 6. Curves I - III refer to B, B+Ba(NO₃)₂ and B + KClO₄ + binder, respectively. The similarity of these curves points to boron as the exothermal component. The heat production is presumably a consequence of a surface oxidation by free oxygen or by the oxidizing agents. The reaction energy amounts to approximately 30 J/g boron. The curve for the complete composition A6 has quite a different shape, exhibiting a maximum after 8 days. The total energy is approximately 50 J/g boron. The width and location of the peak depends on at least two parameters, the humidity and the composition density. The different shape and

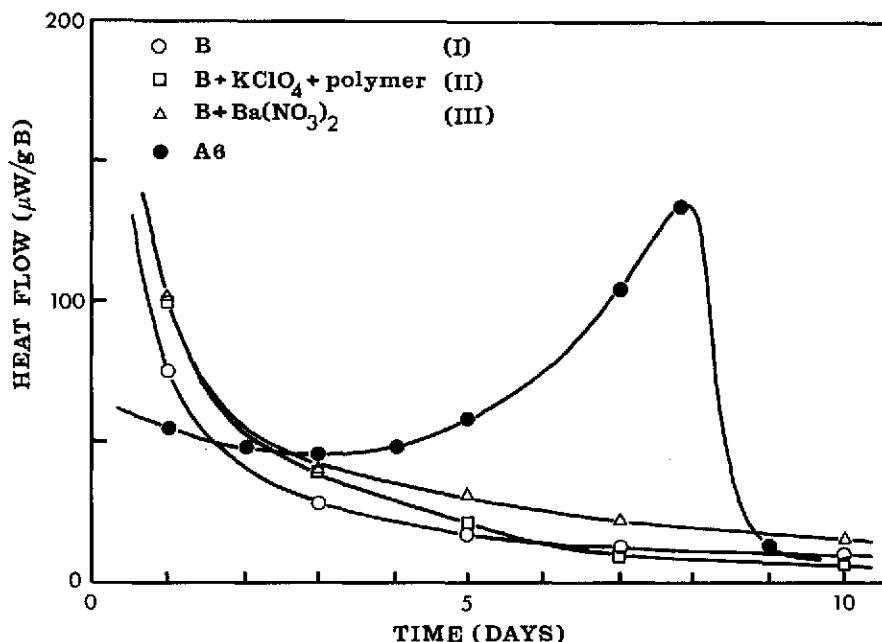


Fig. 6. Heat flow curves at 70°C for the system A6 (igniting composition) and different combinations of the components.

energy of the A6 curve indicates the presence of combination effects when all components are mixed.

CONCLUSIONS

Microcalorimetric results from a wide range of explosive/plastic combinations show that this method could be successfully applied to compatibility problems. Comparison of experimental and theoretical heat flow curves and total energies calculated from these, together with physical and chemical considerations are used in the interpretation of interaction phenomena and their connection to compatibility. The method is very sensitive and measures all interactions involved at moderately accelerated temperatures.

ACKNOWLEDGEMENTS

We are deeply indebted to Prof. Ingemar Wadsö and Dr. Jaak Suurkuusk, Thermochemical Laboratory, Lund, Sweden, for their further development of their microcalorimeter on our behalf, and for valuable discussions about theory and techniques of calorimetry.

REFERENCES

- 1 R.B. Barendregt, 'Compatibility of Thermite and Polyurethane', PML 1979-37, Report IVA, Rijswijk, The Netherlands, 1979.
- 2 F.G.J. May, J. Hazardous Materials, 2(1978)127-135.
- 3 L. Malotky and H. Heller, J. Hazardous Materials 2(1978)189-195.
- 4 AB BOFORS NOBELKRUT 'Analytical Methods for Powders and Explosives', Bofors, Sweden, 1960.
- 5 J.L.C. van Geel, 'The Self-Ignition Hazard of Nitrate Ester Propellants', Thesis, Delft, The Netherlands, 1969.
- 6 M. Frey, 5th Symposium on 'Chemical Problems Connected with the Stability of Explosives', Sweden, 1979, pp.345-359.
- 7 M. Dreyfus and M. Leveque, 5th Symposium on 'Chemical Problems Connected with the Stability of Explosives', Sweden, 1979, pp.381-392.
- 8 J. Suurkuusk and I. Wadsö, *Chemica Scripta*, in press.